SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Final Staff Report for

PROPOSED AMENDED RULE 1144 – METALWORKING FLUIDS AND DIRECT-CONTACT LUBRICANTS

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

In March 2009, Rule 1144 – Vanishing Oils and Rust Inhibitors, was adopted establishing VOC content limits for vanishing oils and rust inhibitors used during metalworking and metal-forming operations. Vanishing oils are a small subset of metalworking fluids designed to evaporate off shortly after use. Rust inhibitors, more commonly referred to as metal protecting fluids, are inhibitors or preventatives used to prevent the corrosion of metal substrates. However, the vast majority of fluids used during metalworking and/or metal forming operations are lubricants and metalworking fluids. These fluids are used at steel tube and spring manufacturers, steel mills, aerospace manufacturers, automobile part manufacturers and rebuilders, as well as machine shops for broaching, drilling, drawing, heading, honing, forging, milling, stamping, tapping, threading and turning operations.

While EPA Method 24 is the default method for determining VOC content, it is unreliable for semi-volatile materials typically found in lubricants and metalworking fluids. It was decided not to include limits for direct-contact lubricants and metalworking fluids until a more reliable method was validated. Recently, a thermogravimetric analysis (TGA) method was developed and validated by ASTM International. If approved by June 4, 2010, ASTM E 1868-10 Standard Test Method for Loss-On-Drying by Thermogravimetry will be used to determine VOC content. Otherwise, SCAQMD Method 319-10 Determination of Volatile Organic Compounds (VOC) in Metalworking Fluids and Lubricants by Thermogravimetry will be included in the rule and used to determine VOC content. This allows limits to be set for these widely used fluids, facilitating the inclusion of direct-contact lubricants and metalworking fluids into Rule 1144.

Staff proposes the following requirements for Proposed Amended Rule 1144:

- Revise and expand the applicability and purpose sections of the rule to include direct-contact lubricants and metalworking fluids.
- Add and modify definitions for metalworking fluid, metal forming fluid, metal removal fluid, metal protecting fluid (rust inhibitors),metal treating fluid, military specified preservative, precision metal removal fluid, super compliant materials and vanishing oil to enhance the clarity of the rule.
- Establish a VOC limit of 50 grams per liter of material for the use of direct-contact lubricants effective January 1, 2012.
- Establish a VOC limit of 130 grams per liter of material for the use of precision metal removal fluids effective January 1, 2012.
- Establish a VOC limit of 75 g/l for metal forming, metal removal and metal treating fluids effective January 1, 2012.
- Establish a VOC limit of 340 g/l for military specified preservatives effective January 1, 2011.
- Exempt the use of dimethyl carbonate as a cooling solvent in computed numerically controlled (CNC) machines where permeable media are used to maintain a vacuum that holds the part in place during cutting provided that the equipment is enclosed and an exhaust fan discharges the exhaust air from the equipment outside of the building.

- Prohibit the sale of non-compliant direct-contact lubricants and metalworking fluids, except those subject to CARB consumer products regulation found in Title 17 of the California Code of Regulations, beginning at Section 94507.
- Allow direct-contact lubricants and metalworking fluids manufactured prior to January 1, 2012 to be sold or applied until July 1, 2012.
- Require containers for direct-contact lubricants and metalworking fluids to display the date of manufacture and VOC content as supplied.
- Establish a streamlined record keeping system for metalworking fluids and direct-contact lubricants subject to the rule.
- Require annual quantity and emissions reporting from manufacturers and suppliers of metalworking fluids and direct-contact lubricants sold or used in the District.
- Incorporate a TGA method, ASTM E 1868-10 Standard Test Method for Loss-On-Drying by Thermogravimetry, for determining VOC content.

If approved, the proposed rule amendments would fully implement control measure CTS-01 in the 2007 Air Quality Management Plan.

The proposed future limits would reduce emissions by 0.86 tons per day at an estimated one-time cost of $2.5 million dollars to conduct laboratory testing prior to January 1, 2012. The overall cost-effectiveness of the proposed amendment is estimated to be $796 per ton of VOC emissions reduced based on discounted cash flow (DCF) analysis. Staff estimates that more than 7,000 shops will be subject to the proposed rule.

BACKGROUND

In March 2009, Rule 1144 was adopted establishing VOC content limits for vanishing oils and rust inhibitors, more commonly known as metal protecting fluids, used during metalworking operations. Vanishing oils and solvent cutback metal protecting fluids consist entirely or nearly entirely of mineral spirit type solvents. While they are a significant source of VOC emissions, they represent only a small fraction of the overall volume of fluids used by machine shops. The bulk of the volumes used are metalworking fluids and lubricants. Unlike vanishing oils and solvent cutback metal protecting fluids, these fluids mainly consist of semi-volatile compounds for which a reliable VOC content test method was not established in March 2009. However, recently a thermogravimetric analysis (TGA) method was developed and validation is complete. This allows limits to be set for these widely used fluids, facilitating the inclusion of lubricants and metalworking fluids into Rule 1144.

Over 7,200 facilities, predominantly small businesses, use these types of fluids in the South Coast Air Basin. They are classified as fabricated metal product manufacturing [North American Industry Classification System (NAICS) Code 332], machinery manufacturing (NAICS 333), transportation equipment manufacturing (NAICS 336), and petroleum and coal products manufacturing (NAICS 324) sectors in the AQMD. Typical industries using lubricants and metalworking fluids include:

- Aerospace
- Machine Shop (Job Shop)

- Steel Mills
- Auto Rebuild
- Screw Machine
- Steel Tubes (Pipes)
- Steel Springs
- Maintenance
- Captive

Captive machine shops are machine shops located inside of another type of business (aerospace, automotive, etc.) that supports the business but is not the primary aspect of that business.

Lubricants and metalworking fluids are used to reduce heat and friction to prolong the life of the tool, to improve product quality, and carry away debris. Metalworking fluids encompass a broad range of fluids including metal forming, metal protecting, metal removal and metal treatment fluids. Typical metalworking operations include:

Metal Forming

- Drawing - Forming flat sheet metal into "cup-shaped" parts. If the depth of the formed cup is equal to or greater than the radius of the cup, the process is called deep drawing.
- Heading – A metal forging process which involves rapidly punching a blank into a die to form a desired shape without adding heat. Cold heading is most frequently used to produce fasteners such as bolts and screws without adding heat.
- Forging - Shaping metal by using localized compressive forces. Cold forging is done at room temperature or near room temperature. Hot forging is done at a high temperature, which makes metal easier to shape and less likely to fracture. Common forging processes include: roll forging, swaging, cogging, open-die forging, impression-die forging, press forging, automatic hot forging and upsetting.
- Stamping – A process by which sheet metal strips are punched using a press tool which is loaded on a press to form the sheet into a desired shape.
- Wire drawing - Reducing or changing the diameter of a wire or rod by pulling the wire or rod through a single or series of drawing die(s).

Metal Protecting

- Rust Preventative/Inhibitor - Prevention of rust on ferrous materials
- Corrosion Protections - Prevention of corrosion on some nonferrous materials

Metal Removal

- Broaching – Keyway, slots or spline utilized in gear manufacturing
- Drilling – Producing cylindrical holes
- Honing - Manufacture of precision bores to improve the geometry, surface finish and dimensional control of the finished part.
- Milling – A precisely controlled rotating cutter which rotates about the spindle axis and a table to which the workpiece is affixed. The cutter and workpiece move relative to each other, generating a toolpath along which material is removed.
- Tapping – Creating threaded holes in parts or boring into parts and pipelines
- Threading - Thread cutting and thread rolling applications for pipes and bolts
- Turning - Operation that produces cylindrical parts

Metal Treatment

- Quenching – A rapid cooling of parts typically for hardening purposes

The fluids used in the above operations are complex mixtures of a base material (oil), and emulsifiers, anti-weld agents, corrosion inhibitors, extreme pressure additives, buffers (alkaline reserve), biocides, as well as other additives. The base material may be naphthenic, paraffinic or synthetic. Some products contain extreme pressure (EP) additives containing chlorinated, sulfurized, or phosphorus-type extreme pressure ingredients. There are numerous formulations, ranging from straight oils (such as naphthenic and paraffinic petroleum oils) to water-based fluids, which include emulsifiable (soluble) oils and semi-synthetic/synthetic fluids. In general, higher oil content provides better lubricity while higher water content allows more rapid cooling.

- **Straight oil (neat oil) fluids** are refined naphthenic and paraffinic petroleum or vegetable oils. Straight oils are not designed to be diluted with water. Light oils are naphthenic oils with a viscosity of 4.28 centistokes (40 SUS) or lower.
- **Emulsifiable oil (soluble oil) fluids** are combinations of 30 percent to 85 percent straight oils and emulsifiers that may include other performance additives. Soluble oils are diluted with 5 to 40 parts water.
- **Semi-synthetic fluids** contain a lower amount of straight oil in the concentrate (5 percent to 30 percent), more emulsifiers, and 30 percent to 50 percent water. The concentrate is further diluted with 10 to 40 parts water.
- **Synthetic fluids** contain no petroleum oils and may be water soluble or water dispersible. The synthetic concentrate is diluted with 10 to 40 parts water.

In 2006, the AQMD and U.S. EPA Region IX co-sponsored a report by the Institute for Research and Technical Assistance to identify, test and demonstrate alternative low-VOC materials for vanishing oils and rust inhibitors. The final report, entitled Assessment, Development and Demonstration of Alternatives to VOC-Emitting Lubricants, Vanishing Oil and Rust Inhibitors concludes that "alternative low-VOC materials for a variety of different types of metalworking operations are available and cost effective". Thirteen facilities participated in the study that reviewed stamping, honing, cutting, forming and rust inhibitor applications. In each high-VOC application, a low-VOC alternative was demonstrated to have equivalent performance. Some of the participants found that their cost increased with the alternatives, but the majority realized a cost-savings.

PROPOSED AMENDED RULE

Staff proposes the following requirements for PAR 1144:

Purpose and Applicability

The purpose and applicability of the rule will be expanded to include direct-contact lubricants and metalworking fluids. These products represent the bulk of fluids used for metal forming, metal protecting, metal removal and metal treatment operations. Including these products will reduce VOC emissions and provide clarity with respect to applicability for the most widely used metalworking fluids.

Requirements

The proposed rule will establish a VOC limit of 75 g/l of material for metal forming, metal removal and metal treatment fluids effective January 1, 2012. More than 90 percent of these

types of metalworking fluids already in use today are expected meet the proposed limit. Annually, more than three million gallons of straight oil and emulsifiable, semi-synthetic and synthetic metalworking fluids are used that are super compliant (less than 50 g/l) under the applicable test methods. The remainder are light, naphthenic oils with viscosities lower than 5 centistokes at 40°C. Light oils are used by manufacturers and distributors as a blending material along with much higher viscosity lubricants (greater than 38 centistokes at 40°C) to form medium viscosity metalworking fluids (10 centistokes or greater at 40°C). The proposed VOC limit will restrict this practice and require manufacturers and distributors to formulate with higher viscosity oils. Shops utilizing these fluids are not expected to experience any performance or cost impact. According to industry stakeholders, the light oils were used in the blend because the medium oils cost more. Changes in demand have leveled the prices and formulators can now eliminate the light oils without impacting costs.

Precision metal removal fluids will be distinguished from metal removal fluids and a VOC limit of 130 g/l will be established effective January 1, 2012. These fluids are used in carbide grinding machine tools where the manufacturer of the machine tool specifies the viscosity of the fluid. They are also used for machining of aluminum and magnesium in single or multiple spindle automatic machines where the design of the machine prevents the use of water-dilutable metal removal fluids. According to the Independent Lubricant Manufacturers Association (ILMA), approximately 20,000 to 50,000 gallons per year of this material is used in the District.

The proposed rule will also establish a VOC limit of 50 g/l of material for direct-contact lubricants effective January 1, 2012. Direct-contact lubricants differ from general lubricants in that they freely mix with metalworking fluids during the manufacturing process. Direct-contact lubricants have traditionally been formulated with heavier petroleum oils or emulsifiable, semi-synthetic and synthetic compounds with relatively low VOC content. Establishing a rule limit is not expected to require formulation changes or reduce emissions. However, it will prevent certain types of metalworking fluids from being reclassified as direct-contact lubricants to avoid being subject to the proposed regulation.

In addition to using heavier naphthenic oils, manufacturers, distributors and users of metalworking fluids and direct-contact lubricants have several other super compliant alternative technologies available. Paraffinic oils are the most similar alternative technology available for reformulation. Paraffinic base material costs approximately ten percent more than a naphthenic base material and in many cases the current practice of using naphthenic oils may strictly be based on cost. Both naphthenic oils and paraffinic oils are straight petroleum oils with paraffinic oils consisting mostly of n-alkanes while naphthenic oils are mostly cycloalkanes. Performance is unlikely to be impacted by the use of paraffinic oils compared to naphthenic oil as paraffinic oils provide better lubricity, greater oxidation resistance, more water resistance and better compatibility with machinery and parts. However, substantial obstacles may need to be overcome to completely transition away from naphthenic oils. Some fluids are specifically formulated for a particular operation and may contain a complex blend of additives. As some additives are not readily soluble in paraffinic oils, substantial reformulation may be necessary. The types of parts likely to be impacted by the loss of soluble additives are high value parts made from aluminum, stainless steel, copper, brass, and titanium.

Another alternative available is water-dilutable metalworking fluids including emulsifiable, synthetic and semi-synthetic fluids. These fluids are specifically engineered for exclusive application as metalworking fluids. Emulsifiable and semi-synthetic fluids contain some straight oil as well, but all contain advanced additives and chemistries providing equal or superior performance compared to straight petroleum oils. Biocides and anti-foaming agents extend fluid life, reduce maintenance and machine downtime. Additionally, they are heavily diluted with water which improves the cooling characteristics as well. The concentrate costs are eight to ten times higher than straight oil costs but after dilution the overall costs are similar or lower than straight oils. The main drawback is that water-dilutable fluids are not always compatible with the machining equipment. In particular they are not viable alternatives for the single or multiple spindle automatic machines which use a substantial portion of the light naphthenic oils. The market share of super compliant direct-contact lubricants and metalworking fluids is already approximately 44 percent.

Vegetable-based oils are also a potential alternative. They are significantly more expensive, ranging from 2.5 to 4 times the cost per gallon of naphthenic oils. Another potential limitation is that the vegetable-based oil waste stream must be segregated from other oil waste streams because of incompatibility. Despite these drawbacks, vegetable-based oils are used because of the superior cooling properties over naphthenic oils allowing for increased machining efficiency (lower labor costs). In a case study included in the referenced report by IRTA, one shop realized an eleven percent cost savings because of increased machining efficiency. It is estimated that ten percent of the impacted facilities can segregate their waste streams and overcome the high per gallon cost by successfully realizing increased machining efficiency.

Staff will continue to monitor the progress of market penetration with paraffinic, water-dilutable and vegetable-based metalworking fluids through the annual quantity and emission reports required under the proposed rule.

Another modification will be to distinguish military specified rust preservatives from general metal protecting fluids and establish a limit of 340 g/l, effective January 1, 2011. The proposed limit is consistent with Mil-PRF-16173E Class II for solvent cutback corrosion preventatives on military equipment. The higher limit will be restricted to military applications qualified under a military specification. Four of the six manufacturers who provide military specified rust preservatives offer products with VOC content below the proposed 340 g/l limit. This limit will forgo previously expected emission reductions of 0.06 tons per day.

Administrative Requirements

A use and sell-through provision is already included in the rule that allows products manufactured before the effective date of the rule to be sold and used for up to six months after the effective date. With the expanded categories, manufacturers and distributors will be required to display the date or a date code of manufacture on the container beginning January 2012. In addition, the VOC content will be required to be displayed on the container.

Manufacturers and distributors will be required to provide an annual quantity and emission report documenting sales volume and VOC content of metalworking fluids and direct-contact lubricants sold in the District. The information will provide an improved emission inventory and identify opportunities to further reduce VOC limits in applicable fluid categories. The emission

inventory will be improved as VOC values are determined for the many thousands of metalworking and direct-contact lubricant formulations, leading to enhanced planning and AQMP development. Staff will work with interested stakeholders to develop reasonable content and format requirements for the annual report, protective of confidential business information (to the extent allowable under District Public Records Act Guidelines). Staff anticipates the completion of this effort no later than September 30, 2010. The other portion that staff will work with interested stakeholders is the product listing (i.e., product name and/or code), the technology used in the product (i.e., paraffin, water-based, synthetic, bio-based, etc.) and other such items to get a better understanding of the product offering and trend in sales over the three year period. Other additional information would be the category the product falls under, as currently included in Table A, the recommended dilution ratio (or range) if any, and an indication as to why a product with a higher than listed VOC limit was sold into or within the District (i.e., under sell through provision; specific exemption; emission control system use; or other).

Recordkeeping Requirements

Many of the facilities subject to the provisions of this rule are small businesses with limited interaction with the District. Those small facilities with operations and equipment that do not use paints, coatings, solvents or adhesives and do not require permits with the District are unlikely to have had experience in keeping daily records. The proposed rule includes recordkeeping provisions. Users of fluids subject to the rule will be required to maintain a list of VOC containing products subject to the rule. In addition, they will be required to track usage of these products on a monthly basis. Alternatively, facilities may opt to maintain records per Rule 109 - Recordkeeping for Volatile Organic Compound Emissions. Products with VOC content below 50 g/l will be considered "super compliant" materials and will be exempt from recordkeeping. This exemption only applies at facilities that do not exceed four tons of VOC emissions in any calendar year, determined by annual purchase records.

Manufacturers and suppliers will be required to keep laboratory reports and/or VOC calculation information used to determine VOC content of products sold. These documents will be used to verify product VOC labeling, including claims of super compliant status.

Test Methods and Procedures

VOC content will be determined by thermogravimetric analysis (TGA). This method has been validated using ASTM E691 - 05 Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method. The time and temperature parameters were determined by comparing the test results to an evaporation study conducted by W.S. Dodge Oil where three naphthenic oils with viscosities of 4.28 centistokes at 40°C (40 SUS), 9.63 centistokes at 40°C (60 SUS) and 20.50 centistokes at 40°C (100 SUS) were held at 40°C in an oven for six months. A provision to determine specific gravity will be included in the method. ASTM E 1868 – 10 Standard Test Method for Loss-On-Drying by Thermogravimetry will be used to determine VOC content if approved by ASTM International by June 4, 2010. Quality assurance and quality control procedures shall be conducted using SCAQMD Additional Requirements to ASTM Standard Test Method E 1868 - 10 for Metalworking Fluids and Direct-Contact Lubricants. In the event that ASTM International does not approve ASTM E 1868 – 10 by June 4, 2010, SCAQMD Method 319 -10 will be expanded to include both the method and

the quality assurance and quality control procedures and included in PAR 1144, which will be used to determine VOC content. Water content will be determined by ASTM D 4017 (Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method). The water content measured by ASTM D 4017 will be deducted from the volatility measurement in the TGA test when determining VOC content. ASTM D 4017 has approximately a three percent margin of error which becomes critical for coatings with high water content where the water is excluded when determining regulatory VOC content. As the water content increases, the margin of error for the non-excluded portion of the sample increases. However, in this case the water content will not be excluded but instead deducted keeping the margin of error constant. The exempt solvent content shall be determined by SCAQMD Method 303 (Determination of Exempt Compounds)

The default method used for determining VOC content has been U.S. EPA Reference Method 24 (Method 24). Method 24 was designed to determine the VOC content of coatings and inks only. It was not intended to be used for metalworking fluids though there is no other U.S. EPA approved test method other than Method 24 for metalworking fluids. Method 24 determines the VOC content of a product by measuring the water and the non-volatile fraction. The remainder is considered VOC (less exempt solvents). The non-volatile fraction is determined by placing the sample in a forced air over at 110°C for sixty minutes. It became apparent following the review of many Method 24 test results that Method 24 would not be reliable test method for many metalworking fluids and direct-contact lubricants which are largely comprised of semi-volatile constituents. For the same samples tested, Method 24 resulted in VOC readings that were consistently higher than those obtained from the six-month long evaporation study mentioned above. The California Department of Pesticide Regulation (DPR) developed a test method for pesticides which primarily consist of paraffinic oils to address the semi-volatile nature of the oils. Their method requires the sample to be held at 115°C for 60 minutes. However, the sample mass loss must stabilize for an extended (11 hours) but low temperature (55°C) alternative is required. It is expected that there would be little difference between the short term and extended tests.

The DPR method was tested on naphthenic oils but they did not stabilize at 115°C. The extended test was performed but the results differed significantly from the short term test. Additionally, manufactures felt that an 11 hour test would be cost-prohibitive. In response, the Independent Lubricant Manufacturers Association (ILMA), in cooperation with District staff, developed the TGA method as a more reasonable alternative with temperature and duration parameters that would replicate the six-month evaporation rate testing.

An alternative method is SCAQMD Method 313-L – Determination of VOC Hydrocarbon Compounds in Lubricants using a gas chromatograph (GC) equipped with a flame ionization detector (FID). A liquid sample is injected into the GC/FID and the concentrations of the individual compounds that elute prior to methyl palmitate are summed. This method is currently undergoing validation testing and may be included at a later date. Table I below compares the results of three naphthenic oils tests by the different methods.

Table I – Test Method Comparison

Method	HyNap 40 (g/l)	HyNap 60 g/l)	HyNap 100 (g/l)
EPA Method 24	859	515	255
SCAQMD Method 313-L	792	492	250
DPR TGA Method (1hr @ 115°C)	849	284	86
DPR TGA Method (11hr @ 55°C)	425	82	40
TGA (110 min @ 81°C)	718	131	70
Evaporation (180 days @ 40°C)	721	132	70

The samples used in the validation testing for both the Method 313-L and TGA testing were formulated to test the spectrum of fluids subject to the rule and to provide guideposts to establishing the proposed limits. The samples consisted of a high VOC solvent cutback metal protecting fluid; synthetic hydraulic oil; a general purpose cutting and grinding oil; a pre-diluted water based semi-synthetic cutting and grinding fluid; and a lower viscosity aluminum cutting and grinding metalworking fluid. The general purpose cutting and grinding oil reflects the VOC content of a typical metalworking fluid or the fluid used in an old spindle-type machine. The lower viscosity oils are typically used as precision metal removal fluids. The TGA validation test results are included in Appendix A.

The results from the synthetic hydraulic oil and the water based semi-synthetic cutting and grinding fluid, combined with DPR's testing of paraffinic oils demonstrates that super compliant (<50 g/l) alternatives exist. Synthetic and semi-synthetic fluids are nearly completely non-volatile and many are heavily (5 to 40 times) diluted with water further reducing the VOC content. DPR tested twenty six pesticide products which were mostly paraffinic with smaller amounts of naphthenic oils and other compounds. Twenty of the samples were found to have VOC contents below 35 g/l (5% by weight). Three others were below 70 g/l (10%) and the remaining three were considered test outliers. Since direct-contact lubricants and metalworking fluids are mainly base material with a small percent of additives, transitioning the base material from naphthenic oil to paraffinic oil will further reduce VOC emissions.

Exemptions

The expansion of the rule to include direct-contact lubricants and metalworking fluids will be reflected in the exemptions section of the rule. Where "vanishing oils and rust inhibitors" were named in general terms, they have been replaced with "metalworking fluids and direct-contact lubricants". Specifically all fluids subject to the rule do not have to meet the labeling and sales prohibition requirements if they are sold as consumer products subject to the California Air Resources Board consumer products regulation found in Title 17 of the California Code of Regulations, beginning at Section 94507. Additionally, working fluids subject to the rule are exempt from the sales prohibition of the rule if they are to be sold and used outside of the District. Finally, all fluids applied to avionics and assembled aircraft are exempted.

An exemption has been included for fluids that have a VOC content of 50 g/l or less. These materials will be considered "super compliant" and be exempted from record keeping. This will limit unnecessary tracking of super compliant and non-VOC materials and through an anticipated increased demand, provide an incentive to manufacturers to provide additional super compliant materials to users.

An exemption has been included to allow the use of dimethyl carbonate as a cooling solvent in computed numerically controlled (CNC) machines where permeable media are used to maintain a vacuum that holds the part in place during cutting provided that the equipment is enclosed and an exhaust fan discharges the exhaust air from the equipment outside of the building. This type of use is very limited in terms of equipment and volume, and based on a risk assessment, has acute or chronic health impacts well below the threshold of significance. In addition any potential worker exposure has been minimized.

EMISSION INVENTORY

The emission inventory for the proposed rule was done by reviewing national sales and comparing the number of shops nationally versus the number of shops in the South Coast Air Basin (Basin). Additionally, a survey of local manufacturers and distributors was conducted.

The overall national inventory of metalworking fluids was taken from the International Lubricant Manufacturers Association (2003). National sales were 117.2 million gallons. EPA estimates 10.2 percent of the fabricated metal industry are located in California in its Fabricated Metal Sector Notebook (1995). According to listings in the California Manufacturers Register, the Basin accounts for approximately 70 percent of the industry in California. This would indicate that 8.3 million gallons of MWF were sold in the Basin (see Table II).

Table II – Ratio of National Sales to South Coast Air Basin Sales

Metalworking Fluid	Amount Sold Nationwide (millions of gallons/year)	Amount Sold in California (millions of gallons/year)	Amount Sold in South Coast (millions of gallons/year)
Straight	27.3	2.8	2.0
Soluble	49.3	5.0	3.5
Semi-Synthetic	21.7	2.2	1.5
Synthetic	18.9	1.9	1.3
Total	117.2	11.9	8.3

To supplement these estimates, in 2006, the AQMD conducted a survey of local manufacturers, distributors and users of metalworking fluids and direct-contact lubricants. The survey data indicated that those local manufacturers and distributors annually sold 4.1 million gallons of lubricants (including direct-contact lubricants), metalworking fluids (excluding metal protecting fluids), metal protecting fluids (rust inhibitors) and solvent. Presumably, the solvents are used as vanishing oils, metal protecting fluids, for thinning other metalworking fluids or cleaning. Solvents used for cleaning application subject to Rule 1124 were removed from the inventory. The sales weighted average VOC content was determined using TGA robustness testing, TGA simulation analysis, TGA validation testing results and a limited number of products testing using the TGA test results. Table III summarizes the AQMD survey, the sales weighted average (SWA) VOC content and total calculated VOC emissions from each fluid.

Further testing by manufacturers and distributors complying with the VOC labeling requirement, in conjunction with annual quantity and emission reporting, will improve the emission inventory.

Table III – Surveyed Emission Inventory

Metalworking Fluid Type	Volume Surveyed (thousand gallons)	Sales Weighted Average VOC Content (g/l)	Total VOC Emissions (tons per day)
Lubricants*	661.0	25	0.19
Direct-contact Lubricants	211.1	25	0.06
Naphthenic-based Metalworking Fluids**	745.5	58	0.49
Heavy Naphthenic-based Oil	727.0	25	0.21
Light Naphthenic-based Oil	128.4	718	1.05
Super Compliant Metalworking Fluids	1,339.7	25	0.38
Vanishing Oil	64.1	710	0.52
Metal Protecting Fluids	140.1	660	1.06
Military Specified Preservatives	15.6	660	0.12
Solvent	167.0	790	1.21
Total	4,119.5	N/A	5.29

*Excludes direct-contact lubricants
**Excludes metal protecting fluids, light and heavy naphthenic-based oils and vanishing oil

Rule 1144, adopted in March 2009, already regulates the emissions from vanishing oils, metal protecting fluids and solvents in the previous rule making activity. The emission inventory, when adjusted for the 2.71 tons per day emission reduction from the already regulated categories, is summarized below in Table IV.

Table IV – Emission Inventory (Existing Rule)

Metalworking Fluid Type	Volume Surveyed (thousand gallons)	Sales Weighted Average VOC Content (g/l)	Total VOC Emissions (tons per day)
Lubricants*	661.0	25	0.19
Direct-contact Lubricants	211.1	25	0.06
Naphthenic-based Metalworking Fluids**	745.5	58	0.49
Heavy Naphthenic-based Oil	727.0	25	0.21
Light Naphthenic-based Oil	128.4	718	1.05
Super Compliant Metalworking Fluids	1,339.7	25	0.38
Vanishing Oil	64.1	50***	0.02
Metal Protecting Fluids	140.1	50***	0.09
Military Specified Preservatives	15.6	50***	0.01
Solvent	167.0	50***	0.08
Total	4,119.5	N/A	2.58

*Excludes direct-contact lubricants
**Excludes metal protecting fluids, light oil and vanishing oil
*** Established VOC Limit

The proposed rule amendment establishes VOC limits for direct-contact lubricants, metal forming, metal treatment and metal removal fluids, including a subcategory of metal removal fluids called precision metal removal fluids. Such limits would reduce emissions from light oils used in metalworking fluids and precision metal removal fluids.

Staff notes that according to industry stakeholders, naphthenic metalworking fluid sales declined significantly, by approximately 40 to 50 percent, since the survey was conducted, due to economic recession, business closures and a general transition into lower-VOC products. Staff recognizes that the use cycle is dependent on external forces, but cannot conclude that the decline in sales will be permanent.

EMISSION REDUCTIONS

The proposed rule will establish a VOC content limit of 50 g/l for direct-contact lubricants, 75 g/l for metal forming, metal removal and metal treatment fluids and 130 g/l for precision metal removal fluids, effective January 1, 2012. The impact of these limits would be to restrict the use of light oils in metal removal fluid blends. This would impact about three percent of the metalworking fluids currently used. Industry sources estimate that 20,000 to 50,000 gallons of light oil are used as precision metal removal fluids while the remainder are used as blends in general metalworking fluids. To be conservative with respect to emission reduction, the upper range of the volume estimate of precision metal removal fluids (50,000 gallons) is used because of the higher VOC limit proposed. The distribution is noted in Table V below.

The proposed amended rule also includes a limit for military specified preservatives used in a military application. The previous rule making activity provided a temporary exemption with the assumption that the military specified preservatives could meet the limit for general rust inhibitors. This limit will forgo previously expected emission reductions of 0.05 ton per day.

Table V – Emission Reductions Effective 2012

MWF Type	Volume Surveyed (thousand gallons)	Sales Weighted Ave VOC Content (g/l)	Proposed VOC Content	Percent Reduction	Total VOC Emission Inventory (tons per day)	Total VOC Emission Reduction (tons per day)
Lubricants	661.0	25	50	0%	0.19	0.00
Direct-contact Lubricants	211.1	25	50	0%	0.06	0.00
Naphthenic-based Metalworking Fluids*	745.5	58	75	0%	0.49	0.00
Heavy Naphthenic-based Oil	727.0	25	75	0%	0.21	0.00
Light Naphthenic-based Oil (metalworking)*	78.4	718	75	89%	0.64	0.57
Light Naphthenic-based Oil (Precision Metal Removal)	50.0	718	130	82%	0.41	0.34
Super Compliant Metalworking Fluids*	1,339.7	25	50	0%	0.38	0.00
Vanishing Oil	64.1	50	50**	0%	0.02	0.00
Metal Protecting Fluids	140.1	50	50**	0%	0.09	0.00
Military Specified Preservatives	15.6	340	340***	N/A	0.01	<0.05>
Solvent	167.0	50	50**	0%	0.08	0.00
Total	4,119.5	N/A	N/A		2.58	0.86

*Excludes metal protecting fluids
**Existing limit
***Previous limit was 50 g/l

The adoption of the proposed VOC limits would result in 0.86 tons per day of VOC reduced. As summarized in the table above, emission reductions are anticipated from light-oil and precision metal removal fluids only, that comprise just a little more than 3.06% of the total volume of direct-contact lubricants and metalworking fluids surveyed, but represent 40.7% of the total remaining emissions from this source category. The control efficiency from these two categories is estimated to be 86.7%.

COST AND COST-EFFECTIVENESS

The transition away from light oil metalworking fluid blends to medium viscosity straight cut oils will have no impact on cost. According to industry stakeholders, light oils were previously

used because they were lower cost than heavier oils, but changes in demand have equalized the price over the past few years.

There is also no expected increase in cost from allowing the use of military specified preservatives. The previous rule making activity accounted for a cost increase that will no longer be necessary.

Likewise, the previous rule making activity accounted for testing costs to determine VOC content. However, those costs were limited to vanishing oils and metal protecting fluids (rust inhibitors). Encompassing direct-contact lubricants and metalworking fluids will greatly expand the number of products that potentially need to be tested. Laboratory testing using the TGA method is estimated to cost $250 per sample. Manufacturers and distributors offer hundreds of products each. Many of those are similar with slight variations on the additives incorporated in the product. Manufacturers and distributors may be able to test some subset of products and be able to calculate the VOC content of their remaining products. Others will insist on testing every product to insure rule compliance. Conservatively assuming that there are 10,000 applicable products and every product would be laboratory tested at $250, there would be a one-time cost of $2.5 million. Most containers use computerized labels that can be altered by simple reprogramming. The cost to alter those labels is considered negligible. Likewise, the generation of an annual sales report by the several dozen manufacturers and suppliers of applicable fluids is also considered to be negligible. These costs are noted in the Socioeconomic Assessment.

The proposed limits would reduce emissions by 0.86 tons per day (313.9 tons per year) at an estimated cost of $2.5 million dollars for the first year. Using a DCF methodology, the future cash flow is discounted over a given period of emission reductions to determine cost effectiveness. In this case, we evaluate the one-time cost of testing over a period of ten years. The overall cost-effectiveness of the proposed amendment using this methodology is estimated to be $796 per ton of VOC emissions reduced (see Table VI below).

Table VI – Cost-Effectiveness

Cost	Emission Reduction over 10 year period	Cost-Effectiveness
$2.5 million	3,139 tons	$796/ton

INCREMENTAL COST-EFFECTIVENESS

Under Health and Safety Code Section 40920.6, the AQMD is required to perform an incremental cost analysis when adopting a Best Available Retrofit Control Technology (BARCT) rule or feasible measure required by the California Clean Air Act. To perform this analysis, the AQMD must (1) identify one or more control options achieving the emission reduction objectives for the proposed rule, (2) determine the cost effectiveness for each option, and (3) calculate the incremental cost effectiveness for each option. To determine incremental costs, the AQMD must "calculate the difference in the dollar costs divided by the difference in the emission reduction potentials between each progressively more stringent potential control option as compared to the next less expensive control option."

Proposed Amended Rule 1144 implements Control Measure CTS-01 from the 2007 Air Quality Management Plan. Because Control Measure CTS-01 is intended to meet feasible measure requirements under the California Clean Air Act, an incremental cost analysis is required and is presented in this section.

Two alternative options were evaluated including two more stringent standards. The first alternative examined was to require all lubricants, metalworking fluids and rust inhibitors to meet a VOC content limit of 25 g/l. Similar low-VOC formulations would be utilized but machine operators would have to monitor the fluids to ensure that evaporation or contaminants did not make the fluid non-compliant. The second alternative required all fluids to meet a 50 g/l VOC limit effective in 2015. While industry has been cooperative in providing available information, they cannot provide reformulation cost data at this time. Based on the limited information available, the District estimates the limits effective in 2015 would result in price increases by up to 20%. This estimation methodology is consistent with previous cost analyses where reformulation cost data is not available. Using this methodology, the alternative paraffinic based metalworking fluid used to comply with the 50 g/l and 25 g/l is expected to have an average cost of $5.52 per gallon, an increase of $1.22 over the current average price of naphthenic metalworking fluids. The annual cost of fluid reformulation would be $1.1 million (see below).

Table VII – Cost Increase per Gallon of Material

Total Volume of Impacted Metalworking Fluids	Increased cost per gallon	Total Annual Cost
873,900 gallons	$1.22	$1.1 million

To meet the 25 g/l limit, additional labor costs are included for fluid users to track water evaporation to ensure water-dilutable fluids remain below 25 g/l.

The incremental cost analysis indicates that all of the alternatives considered have an overall cost-effectiveness comparable to other adopted VOC regulations. However, the incremental benefit gained by lowering the limits to 50 or 25 g/l is not cost-effective ($23,182 and $35,351 per additional ton reduced respectively) because of reformulation and additional labor costs.

Table VIII – Incremental Cost-Effectiveness

VOC Limit (g/l)	Emission Reductions (tons per year)	Additional Annualized Cost (million)	Incremental Cost ($ per additional ton reduction)
25 (all categories)	473.0	$5.4	$35,351
50 (all categories)	361.4	$1.4	$23,182
Current proposal	313.9	$0.3	N/A

COMMENTS AND RESPONSES

This section reflects the public comments received during working group meetings, the public workshop held February 10, 2010, the working group meeting held January 28, 2010 and subsequent meetings, as well as staff responses to those comments.

Comment 1
How can we ensure that Method 24, the test method listed in the rule, is not used to determine VOC content for purposes of compliance with the 300 g/l VOC limitation for rust inhibitors pending finalization of a new, valid test method?

Response
VOC content will be determined by thermogravimetric analysis (TGA), ASTM Method E 1868-10 Standard Test Method for Loss-On-Drying by Thermogravimetry, at 81°C for 110 minutes. U.S. EPA Method 24 will not be used for any fluid category VOC determination in Rule 1144.

Comment 2
Does the District interpret Rule 109 to apply to all such materials that may be covered by Rule 1144, or only those that are "adhesives, coatings, solvents, and/or graphic arts materials" as specified in Rule 109?

Response
The recordkeeping requirements have been clarified in the proposed amended rule. Specifically, fluids subject to the rule may be tracked using procedures specified in Rule 109 or with the streamlined process included in PAR 1144.

Comment 3
Some companies report that District inspectors who have visited their facilities indicate that Rule 1107's "coating" requirements currently apply to rust inhibitors (metal protecting fluids), despite the fact that Rule 1144 addresses metal protecting fluids (rust inhibitors) more specifically. This raises compliance issues currently as well as after January 1, 2010. Can the District confirm that Rule 1107 - Coating of Metal Parts and Products does not apply to metal protecting fluids?

Response
There is possible overlap in requirements for some operations, particularly metal protecting fluids, to be covered under both Rule 1107 and Rule 1144. It is District policy for the most specific rule to take precedence. Therefore, Rule 1144 will be used to determine compliance of metal protecting fluid use.

Comment 4
Can the District confirm that Rule 442 - Usage of Solvents does not apply to metal protecting fluids?

Response
Rule 442 requirements are limited to operations that are not subject to a Regulation XI rule. Any operation subject to Rule 1144 (a Regulation XI rule) would therefore not be subject to Rule 442.

Operations specifically exempted from Rule 1144 (i.e. metal protecting fluid used on avionics or assembled aircraft) would be subject to Rule 442.

Comment 5
Can companies using rust inhibitors (metal protecting fluids) utilize the exemption from District permits pursuant to Rule 219(l)(6) (coating applications)? What method shall be used to determine emissions?

Response
Companies utilizing metal protecting fluids that do not exceed the provisions of Rule 219(l)(6) can qualify for exemption. Emissions shall be determined using ASTM Method E 1868-10 Standard Test Method for Loss-On-Drying by Thermogravimetry.

Comment 6
The terminology used for describing products and processes subject to the rule should conform to government and industry standards. Metalworking fluids should cover a broad range of metal removal, forming, protecting and treating operations. "Soluble oils" should be called "Emulsifiable oils".

Response
Staff agrees that the established Occupational Health and Safety Administration (OSHA) terminology will be most familiar to the affected parties. Therefore, the terminology in the rule will be made consistent as recommended. Metalworking fluids will be further distinguished as metal forming, metal protecting, metal removal and metal treatment fluids. Most fluids subject to the rule will have some protective properties but the metal protecting fluid category will refer to products that are used independently of the metal forming, removal or treating applications.

Comment 7
ILMA supports the inclusion of the TGA method for determining VOC content. ILMA recommends that the actual reference to the TGA method in the final rule be ASTM E 1868 - 10, *Standard Test Method for Loss-On-Drying by Thermogravimetry*.

Response
The test method referenced will be included in the final rule provided that it has been approved by ASTM prior to the final hearing for Rule 1144. Otherwise, SCAQMD Method 319-10 Determination of Volatile Organic Compounds (VOC) in Metalworking Fluids and Lubricants by Thermogravimetry will be used to determine VOC content. SCAQMD Method 319-10 incorporates all of the procedures and parameters reflected in the efforts of the laboratory subcommittee and referenced in ASTM E 1868 – 10.

Comment 8
AQMD should terminate further work on the development of SCAQMD Method 313-L – Determination of VOC Hydrocarbon Compounds in Lubricants. AQMD staff has not consulted with industry stakeholders and has refused to subject the test method to the same validation under ASTM E691 as the TGA method. AQMD has purchased and used the TGA equipment in its laboratory and should preserve its limited resources by terminating further efforts to develop

Method 313-L. {A more detailed discussion of comments and responses regarding SCAQMD Method 313-L is included in Appendix B.}

Response
AQMD staff has provided updates and test results to industry stakeholders via the Rule 1144 Laboratory Sub-Committee. One of the participating laboratories in the validation process is an ILMA-member company. As ILMA is well aware, the method is going through the identical ASTM E691 validation process as the TGA method although it has not yet been able to achieve the agreed upon validation criteria. Method 313-L has value for determining VOC content for high water content samples. However, until the validation criteria have been met, it will not be included in the rule. This commitment, and staff implementation to date, is reflected in the adopting Resolutions in the March 6, 2009 Public Hearing.

Comment 9
AQMD has overstated the emission reductions for PAR 1144. AQMD is relying on outdated sales data. AQMD improperly assumes that all VOCs contained in low-VOC materials are emitted. Many of these materials do not volatilize under normal conditions of use. ILMA has provided a more accurate estimate of VOC reductions based on more appropriate values for sales weighted average (SWA) VOC content of naphthenic oils and light oils. Naphthenic-based Metalworking Fluids should be just under 60 g/l after including additives. Similarly, based on current sales data, the SWA of "Light Oil" should be 500 g/l, rather than 718 g/l. The above adjustments are based upon more recent sales data as well as forecasted "no growth" in manufacturing in the South Coast Basin. Further ILMA believes that the expected VOC reductions are over estimated because they do reflect actual in-use conditions. VOC emissions that may exist generally condense and subsequently settle on machines, floors and building superstructures.

Response
The District is using survey data of sales from manufacturers and distributors between 2004 and 2006. The survey data was used to determine emission inventory and emission reductions when Rule 1144 was adopted last year. Recent data provided by industry does suggest lower sales volume most likely associated with the recent economic downturn. However, there is no evidence to suggest that the downturn is permanent resulting in a "no growth" forecast. Recent TGA test results suggest lower sales weighted average VOC contents for metalworking fluids and direct-contact lubricants and those averages have been adjusted accordingly. However, there is no evidence suggesting that light oils used for blending includes additives or heavier oils that might lead to a lower sales weight average VOC content. With respect to light oils, the original sales weighted average VOC content will be retained. Based on comments received, the District has re-evaluated the inventory from the survey and is including the full volume of light oils reported for developing the emission inventory.

Comment 10
We recommend establishing a 50 g/l limit for direct-contact lubricants effective 2012 and eliminating the 2015 limits entirely. Emission reductions are minimal while the increased costs will impair the competitiveness of Southern California machine shops and aerospace facilities. Any decrease in competitiveness will lead to lost manufacturing jobs.

Response
A 50 g/l limit will be established for direct-contact lubricants and the 2015 limits will be removed from the rule. Uncertainty in sales weighted average VOC content for some metalworking fluids and reformulation costs suggest that more study is necessary. To facilitate this, the rule will require an annual quantity and emission report to track sales and VOC emissions. This information, along with a technology review, will provide the foundation for determining if future VOC reductions from applicable categories are appropriate.

Comment 11
AQMD has overstated the estimated emission reductions from the 2015 limits and understated compliance costs. AQMD did not take into account front-loaded research and development costs, disposal costs, base oil price volatility, increased recordkeeping costs and customer testing, qualification and approval costs. ILMA conservatively estimates the annual costs to be $2,000,000 or higher. Using ILMA's cost-effectiveness estimates and suggested emission reductions, the cost-effectiveness of PAR 1144 is $19,239 per ton of VOC reduced. At $19,329 per ton makes poor financial sense and the proposed 2015 limits should be withdrawn. ILMA members indicate that the proposed 2012 limits will cause no disruptions or reformulations. AQMD is specifically required by statute to provide cost-effectiveness, including alternatives to the proposed rule and incremental cost-effectiveness which the Preliminary Draft Staff Report does not include.

Response
In presenting cost estimates in the Preliminary Draft Staff Report and in the Public Workshop and working group meetings, staff has requested interested stakeholders to provide cost estimates for research and development activities so they could be included when making a cost-effectiveness determination. Some limited anecdotal evidence has been provided but it is insufficient to make cost-effectiveness determinations. Because of limited reformulation cost information and uncertainty with respect to the sales weighted average VOC content of metalworking fluids, the 2015 limits of the proposed rule has been withdrawn. The 2012 limits for metalworking fluids and direct-contact lubricants will be included and are expected to have little or no cost impacts as noted in the comment above. As required under Health and Safety Code Section 40920.6, the Draft Staff Report does include cost-effectiveness, including incremental cost-effectiveness for rule alternatives based on the 2012 limits only.

Comment 12
AQMD improperly assumes that the change from naphthenic base oils to paraffinic base oils is easy. A wide range of additives do not solubilize and/or respond properly in paraffinic base oils, especially extreme-pressure additives and emulsifiers. Also, a reliable supply of paraffinic oils in not locally available and must be transported by truck or rail from Texas or Louisiana.

Response
While it was noted that some reformulations would be straightforward without the necessity of reformulation, the staff report did recognize that substantial reformulation may be necessary for additives that did not solubilize in paraffinic oils. This is further reflected in staff's request to industry stakeholders to provide reformulation cost estimates. Finally, the proposed limits requiring reformulation were scheduled to occur in 2015 allowing sufficient time for

manufacturers and distributors to incorporate new technologies. However, since the 2015 limits have been withdrawn, the change from naphthenic base oils to paraffinic base oils is no longer necessary.

Comment 13
The proposed recordkeeping requirements are excessive. Contrary to AQMD's assertion, the proposed recordkeeping requirements are not "streamlined". ILMA requests that the water disposal column on the proposed recordkeeping form be eliminated. It suggests that the records allow for a "mass balance" accounting of VOC emissions which would not take into account fluid lost on parts or other loss streams.

Response
The proposed recordkeeping requirements provide the necessary information to document compliance. They are in a more streamlined format than the Rule 109 – Recordkeeping for Volatile Organic Compound Emissions requirements already included in the rule. At the request of industry, either recordkeeping format will be acceptable. There is no requirement to track water disposal or waste disposal for recordkeeping purposes. The proposed rule does require that purchase records be maintained for verification purposes. If a facility chooses to create a "mass balance" of fluid use and loss, it could be done on a completely voluntary basis.

Comment 14
The proposed recordkeeping requirements jeopardize information historically treated as confidential. AQMD's existing procedure for asserting trade secrets should work well for companies that use products covered by the rule. However, it does not protect manufacturers of the products because they are not directly involved in the preparation of the documents that will be submitted to the AQMD. In order to protect manufacturer's trade secrets, manufacturers should have the opportunity to claim trade secret status whenever a document kept by one of its customers is submitted to the AQMD or to implement a coding system for data entry on the document that masks the identity of the manufacturer and product.

Response
Manufacturers and distributors are welcome to ask users of the fluids they sell to request that the information be kept confidential. Only information claimed to be a trade secret at the time of submittal to the District may be treated as a trade secret. [Masonite Corp. v. County of Mendocino A.Q.M.D., 49 Cal.Rptr.2d 639 (1996)]. The District will follow the Guidelines for Implementing the California Public Records Act (Adopted by the Governing Board May 6, 2005). These guidelines are available for review at http://www.aqmd.gov/prr/prag.html.

Comment 15
ILMA acknowledges that other chemistries, notably vegetable-based lubricants, can provide a low-VOC alternative for some formulations. However, mixing vegetable lubricants with mineral lubricants (naphthenic or paraffinic), results in a waste solution mixture that has no recyclable value. It will take years to build an infrastructure to effectively handle either straight vegetable oil or comingled vegetable and mineral oil products.

Response
Vegetable-based lubricants are an option for users seeking a super compliant alternative to naphthenic-based lubricants. Other options include water-dilutable fluids, including emulsifiable oils and semi-synthetic and synthetic fluids, and paraffinic-based lubricants. Users are not required to select any particular option and likely will choose options that maintain or exceed performance requirements, are cost-effective and have an infrastructure in place to handle waste solutions. As demand for super compliant and environmentally preferable materials grow, it is expected that technological barriers will be overcome allowing for greater use over a wider range of applications.

Comment 16
Case studies have been provided which demonstrate a pattern of implementation costs that can be expected for each and every large user of these fluids if reformulation is required for any reason at all. Formulation changes made to improve the process save customers money while reformulation to an arbitrary standard not directly related to performance or improvements have great cost impacts. We think it is fair to assume costs proportionately similar to these for all customers who need reformulating, testing and re-approvals.

Response
After reviewing the detailed costs, the 2015 limits that would require reformulation, testing and re-approvals were withdrawn. The 2012 limits proposed in the rule do not require reformulation, testing or re-approvals. Those limits have been found to be cost-effective and remain in the proposed rule.

Comment 17
We believe that Pale Oil 100 (100 SUS @ 100°F or 22 cSt @ 40°C) is needed for our formulations. Many customers buy it without additives or use it as the basestock. The limits proposed for 2015 would require a change to paraffinic basestock, with all of the attendant costs and difficulties of reformulating, testing and re-approvals. We see no sense in mandating such a monumental change in products for a few hundred pounds per day of emission reductions.

Response
The proposed limit effective in 2012 will allow the use of Pale Oil 100 type fluids to be used. As stated earlier, the 2015 limits have been removed from the proposal. Staff will continue to evaluate costs associated with reformulation, sales and emission reduction potential to determine if further VOC limit reductions are feasible.

Comment 18
We recommend a tightly proscribed "Precision Metal Removal Fluid" category limited to specific applications of aluminum machining and carbide grinding. Slightly lighter viscosity oil mitigates contamination with aluminum oxide and excess loss on chips resulting in poor cuts and reduced tool life. For many years a common practice has been to use solvent previously used for cleaning as a diluent for aluminum cutting oil. By allowing the use of slightly lighter viscosity oil, the District will realize extra, unanticipated VOC reductions by the elimination of this practice.

Response
A "Precision Metal Removal Fluid" category has been included in the proposed rule. The VOC limit proposed will allow 60 SUS @ 100°F type oils to be used in fluids used for carbide grinding machine tools where the manufacturer of the machine tool specifies the viscosity of the fluid or for machining of aluminum in automatic lathes where the design of the machine prevents the use of water-dilutable metal removal fluids. The proposed limit will curtail the use of solvent used as diluents in these applications.

Comment 19
I find it difficult to comprehend how my use of a non-volatile fluid in our 3 man shop will affect the air quality. I suggest you create a size threshold of some sort to exempt a shop of our size from whatever recordkeeping scheme is imposed.

Response
The recordkeeping provisions of the rule have been streamlined because of the nature of the machine shops using the fluids. Most are small businesses using fluids that have little or no VOC. Thus a provision in the rule specifically exempts small shops (emitting less than 4 tons of VOC per year) from keeping records of non-volatile fluids (those with VOC contents less than 50 g/l).

Comment 20
We are a two person prototype machine shop. We are asking that the rule have minimal financial impact on our company. Please apply any fees based on annual usage rather than per business. We use 5 gallons per month of water soluble coolant and should not pay the same fees as someone who uses or emits much more. Many machine shops have closed and further financial burdens should not be imposed.

Response
There are no direct fees associated with the proposed rule. Facilities emitting over four tons per year of VOC emissions would be subject to annual emission reporting and fees. However, shops using super compliant water soluble coolant would have to use many thousands of gallons per year to reach this threshold. Additionally, water soluble coolants typically have VOC contents below 50 g/l and the rule exempts super compliant fluids from recordkeeping requirements. In the two person shop scenario described, the only likely change for the machine shop would be that the water soluble coolant container would include VOC content information and a date code. No process changes, no recordkeeping and no fees are expected to impact this shop.

Comment 21
We provide alternative and fully compliant non-petroleum technology to the local manufacturing community. We are pleased to say we can deliver compliant products to the market; products that are both functionally effective and in most cases cost neutral.

Response
We encourage you to provide specific case studies and cost information regarding your successes in transitioning shops to super compliant non-petroleum alternatives. The District will continue to evaluate the opportunity to further reduce emissions from these processes and information

regarding successful conversions will be highly beneficial. As noted in the staff report, several alternative technologies show great promise and it is anticipated that their market share will grow as users seek super compliant and environmentally preferable alternatives to petroleum products. This is particularly true as reformulation costs decrease, machines are specifically designed to use alternatives and infrastructure is developed to better utilize the alternative fluids.

Comment 22

We do realize that a new survey needs to be done on the emissions inventory and we don't have any data to give, so we can't contradict any existing data. But, we do agree that we should probably, until 2011 or mid 2011 where the first part of the rule of 1144 comes in to place, let's do a formal survey. ILMA, our trade association, will participate with AQMD as much as we can and give as much data we have collected. What we are asking, and it looks like we have some general concurrence from AQMD, is to have a symposium here at this headquarters. We want to bring individuals from the United States, if not around the world, to discuss this new technology. We will have challenges. We don't think any of the challenges are insurmountable. But the only way to hear them out is to bring the experts in here. And our trade association has access to these individuals and has the advertising on the road to help get those people to come here. And again we have some concurrence that that's a good idea and we support that fully.

Response

We concur that a survey and report are necessary and therefore PAR 1144 includes paragraph (f)(3) that includes an annual quantity and emissions report requirement by manufacturers and suppliers that sell metalworking and direct-contact lubricants into or within the District. This reporting requirement will be for annual sales and VOC content and we will work with interested stakeholders on the format of the survey. The additional survey items can include information the parties agree gives the District a better understanding of product trends in the District as documented in the Board resolution. Staff also concurs that a symposium to be held at the District will be beneficial to further get a better understanding of low-VOC technology under development or already commercialized.

Comment 23

We use a Datron CNC machine to fabricate metal parts which uses denatured ethyl alcohol as a machine coolant. For more than twelve months, we have tried a variety of substitute coolants. We have found just one solvent, dimethyl carbonate, that meets our requirements. We hereby request the SCAQMD to classify dimethyl carbonate as an exempt compound. As an alternative, we ask that an exemption be made in Rule 1144 for cooling solvents used in CNC machines where permeable media are used to maintain a vacuum that holds the part in place during cutting.

Response

An exemption has been included in PAR 1144 to allow the use of dimethyl carbonate as a cooling solvent in computed numerically controlled (CNC) machines where permeable media are used to maintain a vacuum that holds the part in place during cutting. The exemption further requires that the equipment be enclosed and emissions be vented and discharged outside of the building. This type of use is very limited in terms of equipment and volume, and based on a risk assessment, has acute or chronic health impacts well below the threshold of significance. In addition any potential worker exposure has been minimized.

Comment 24
To this date we can only speculate with little accuracy the true VOC of a "neat" oil. Is there an estimate on how much money and time has been invested in determining a VOC test method? How can a rule be in place when it cannot be tested? What is the real value in testing a low VOC oil?

Response
Through the efforts of the laboratory subcommittee formed to address the question of VOC content of metalworking fluids and lubricants, a public/private partnership has been successful in developing a repeatable and reproducible method to determine the VOC content of these fluids. The subcommittee met on more than half a dozen occasions and both District and private laboratories conducted several rounds of testing. While this has been a considerable investment, it has lead to significant and cost effective emission reductions.

Comment 25
Little study has been performed on oils taken from working situations. Is the AQMD and industry confident that they can test these "real world" oils?

Response
The test method developed is robust enough to test products taken directly from field use. The method can test the wide range of fluids used for metalworking and lubricant applications including those with specialized additives.

Comment 26
Whether a customer is military or commercial, specifications for a rust preventative or sealant will not typically change. If a change is required by the regulation, the business will go to someone else. If a customer cannot send in a request for quote with a high VOC rust preventative without violating the solicitation provision in the rule, we will lose business.

Response
Low-VOC metal protecting fluids have been developed that meet or exceed the performance requirements included in military and commercial specifications. Businesses will continue to be able to satisfy their customer's needs for adequate corrosion protection. Only the direct requirement to use a high-VOC product constitutes a violation of the solicitation provision.

Comment 27
What is the real cost and true value of the proposed regulation? The loss of high performance oils is a cost and lost revenue for the end user and the District.

Response
The cost and cost-effectiveness of the rule is included in the staff report. Furthermore, a socioeconomic analysis has been conducted to evaluate the impact of the proposed rule on the local economy. The proposed rule is cost effective and overall there would be few job impacts of the proposed amendments on the local economy. For those fluids impacted by proposed VOC limits, adequately performing low-VOC alternatives have been identified.

Comment 28
"Turning" comprises at least half of all metal removal applications and should be included in the definition of metal removal.

Response
"Turning" has been included as an example in the metal removal definition.

Comment 29
It continues to be our understanding that the proposed limits are not necessarily achievable for oils if the refiner uses a lighter oil to blend to achieve appropriate viscosity. Enforcement should be addressed at the oil manufacturer, as labeled, not the shop level.

Response
Usually only small amounts of light oil are used for base stock adjustments and should not significantly change the VOC content of the oils. Manufacturers and suppliers of blended fluids are required to label the container with accurate VOC content, including base stock adjustments. It is easily calculable to determine the VOC content of a base stock oil with a known amount of light oil added for viscosity adjustment.

Comment 30
The phrase "used in an emission control system" is vague and non-definitive. Please consider replacing that statement with "under the control of an emission control system".

Response
The phrase "used in an emission control system" has been changed to "collected and directed to an emission control system" to clarify the intent.

Comment 31
The recordkeeping requirements are excessive and redundant. A listing of materials and quantities should be sufficient.

Response
The proposed recordkeeping requirements provide the necessary information to document compliance. They are in a more streamlined format than the Rule 109 – Recordkeeping for Volatile Organic Compound Emissions requirements already included in the rule. Including a means to verify the listing and quantities reported is critical to determine compliance.

Comment 32
The exemption for avionics and assembled aircraft should be change to the manufacture of parts for avionics and aircraft.

Response
Expansion of the exemption to all aircraft manufacturing is unnecessary. The aerospace industry has been using low-VOC lubricants, metal working fluids and rust inhibitors on the vast majority of their metal working applications. Many tens or even hundreds of thousands of gallons of

metal working fluids used on aerospace products are ultra-low VOC technologies that the staff report identifies as low-VOC alternatives to high-VOC products.

Comment 33
The approval of the VOC test method developed by a public/private partnership between the District and metalworking suppliers has been delayed by ASTM International. We propose that the District delay hearing the rule until ASTM International has approved the method so that it can be incorporated into the rule.

Response
The District has agreed to delay the hearing until June 4, 2010. If ASTM International has not approved the method by that time, staff will recommend that the Board adopt SCAQMD Method 319-10 Determination of Volatile Organic Compounds (VOC) in Metalworking Fluids and Lubricants by Thermogravimetry. Method 319-10 reflects the efforts made by the laboratory subcommittee to develop a reliable and repeatable method for determining VOC compounds of metalworking fluids and lubricants.

Comment 34
The Annual Quantity and Emission Inventory Report should be as narrow as possible. ILMA understands that AQMD staff is drafting a Governing Board resolution that will direct staff to work with interested stakeholders in developing reasonable content and format requirements for the annual report that are protective of confidential business information. However, ILMA requests that the Governing Board's resolution make it explicit to the staff that content requirements of the reporting form should not be used as a "back door" way for AQMD staff to develop regulatory and enforcement information.

Response
The report was included in the regulation because ILMA and industry agreed that more information was necessary to develop an accurate inventory of emissions, particularly sales weighted average VOC content, and to analyze trends of low-VOC products. Staff also concurs that a symposium to be held at the District will be beneficial to further get a better understanding of low-VOC technology under development or already commercialized. All of this information, along with case studies, technology assessments, stakeholder discussion and other research will be used to determine if future regulatory action is warranted.

Comment 35
The applicability section uses such words and phrases as "coining", "blanking", "marquenching", "piercing" and "roll forming" in specifying operations subject to the rule. None of these words or phrases was defined in the rule. CARB believes that without defining these words and phrases, some parts of the rule will be difficult to enforce. To improve clarity and enforceability of the rule, we suggest that those words and phrases be defined.

Response
Coining, blanking, marquenching, piercing and roll forming are included in the rule as examples of metal forming, metal removal or metal treating operations. These operations themselves are defined in the rule and that should be sufficient to provide clarity and enforceability.

Comment 36
The proposed rule introduces a new test method for determining VOC content. EPA is currently reviewing the TGA method.

Response
We look forward to your comments on the test method. EPA is currently reviewing the TGA method. The parameters have been revised to more accurately test naphthenic oils used in the metalworking industry compared to paraffinic oils used in pesticides.

Comment 37
Rule 1144 references SCAQMD Rule 109 for recordkeeping requirements. Because the revised Rule 1144 is adding a test method, we recommend a corresponding section with the new test method be added to Rule 109.

Response
We plan to include the new TGA test method in Rule 109 the next time Rule 109 is opened for amendments.

COMPARATIVE ANALYSIS

Health and Safety Code Section 40727.2 requires a written analysis comparing the proposed rule with existing federal and AQMD regulations. Federal regulations do not regulate VOC emissions from lubricant and rust inhibitor operations. Solid film lubricants, dry lubricative materials and barrier coatings are subject to Rule 1124 - Aerospace Assembly and Component Manufacturing Operations and are not subject to this proposed rule. Similarly, paint and coating intended to completely cure and leave a solid, permanent film to beautify and protect metal surfaces are subject to other coating rules in Regulation XI and are not subject to this rule. Examples include aerospace, architectural, auto body, and metal paints and coatings with applicable VOC limits in Rules 1113 – Architectural Coatings, Rule 1124, Rule 1151 - Motor Vehicle and Mobile Equipment Non-Assembly Line Coating Operations, and Rule 1107 – Coating of Metal Parts and Products respectively.

SOCIOECONOMIC ASSESSMENT

A socioeconomic analysis of Proposed Amended Rule 1144 is included in Attachment G.

CALIFORNIA ENVIRONMENTAL QUALITY ACT (CEQA)

Pursuant to the California Environmental Quality Act (CEQA) and AQMD Rule 110, appropriate documentation will be prepared to analyze any potential adverse environmental impacts associated with the Proposed Amended Rule 1144. Comments received at the public workshop and CEQA scoping meeting will be considered when preparing the CEQA document.

DRAFT FINDINGS UNDER THE CALIFORNIA HEALTH AND SAFETY CODE

Health and Safety Code Section 40727 requires that prior to adopting, amending or repealing a rule or regulation, the AQMD Governing Board shall make findings of necessity, authority, clarity, consistency, non-duplication, and reference based on relevant information presented at the hearing. The draft findings are as follows:

Necessity – State and federal health-based ambient air quality standards for ozone are regularly and significantly exceeded in the AQMD. The reduction of VOC from Proposed Amended Rule 1144 is part of a comprehensive strategy to meet federal and State air quality standards.

Authority - The AQMD Governing Board obtains its authority to adopt, amend, or repeal rules and regulations from Health and Safety Code Sections 39002, 40000, 40001, 40440, 40441, 40702 and 41508.

Clarity - The AQMD Governing Board has determined that Proposed Amended Rule 1144 – Metalworking Fluids and Direct-Contact Lubricants, is written and displayed so that the meaning can be easily understood by persons directly affected by them.

Consistency - The AQMD Governing Board has determined that Proposed Amended Rule 1144 – Metalworking Fluids and Direct-Contact Lubricants, is in harmony with, and not in conflict with or contradictory to, existing statutes, court decisions, federal or state regulations.

Non-Duplication - The AQMD Governing Board has determined that Proposed Amended Rule 1144 – Metalworking Fluids and Direct-Contact Lubricants, does not impose the same requirement as any existing state or federal regulation, and the proposed amendments are necessary and proper to execute the powers and duties granted to, and imposed upon, the AQMD.

Reference - In adopting this regulation, the AQMD Governing Board references the following statutes which the AQMD hereby implements, interprets or makes specific: California Health and Safety Code sections 40001, 40440, and 40702.

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Method 24 – Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings. U.S. Environmental Protection Agency, February 2000.

Laboratory VOC Content Test Method Validation Test Results

Lab	Solvent Cutback Rust Preventative	Synthetic Hydraulic Oil	General Purpose Cutting and Grinding Oil	Pre-diluted water-based semi-synthetic cutting fluid*	Aluminum Cutting Fluid
A	621		60	982	85
B	625		45		90
C	636	2	50	974	72
D	642		50	979	92
E	637		80		145
F	633		56	981	95
G	646		66	981	104
H	608	5	65	929	89

*Before water removed

Comments and Responses Relative to SCAQMD Method 313-L Determination of VOC Hydrocarbon Compounds in Lubricants

The following paragraphs provide staff responses to ILMA's specific comments relative to SCAQMD Laboratory Method 313-L included in their February 17, 2010 letter to the District.

Comment
The use of Gas Chromatography (GC) for the determination of the VOC content of oil- based lubricants and rust preventatives by SCAQMD Method 313-L has proven to be difficult in practice, and with regards to rapidly obtaining results that show inter-and intra-lab reproducibility.

Response
Method 313-L is going through the ASTM E691 validation process although it has not yet been able to achieve the agreed upon validation criteria. Method 313-L has value for determining VOC content for high water content samples. However, until the validation criteria have been met, it will not be included in the rule.

Comment
Running the method as written requires a minimum of 10 hours of instrument time for just one sample. Each additional sample adds at least 90 minutes of additional analysis time. This does not account for the lab hours required to prepare the seven standards, sample duplicates, blanks, and matrix spikes.

Response:
The estimate of "10 hours of instrument time" is overestimated. The reality is that Method 313-L currently takes less time per sample than TGA: 105 minutes versus 140 minutes (including between-sample GC cleanup and TGA cool-down). Although Method 313-L requires more quality control, the ability to run GC autosamplers overnight more than compensates for the additional injections.

ILMA Reply
Method 313-L requires the analysis of seven external standards, a blank, a matrix spike standard, and matrix spike standard duplicate at a minimum for each batch of metalworking fluids analyzed. Additionally, the column must be "baked out" in-between sample runs to minimize sample carry-over. As each run is approximately 45 minutes, and assuming one sample is analyzed in duplicate, this works out to 13 runs x 45 minutes = 9.75 hours. Good analytical practice demands that all standards are run for every batch of samples tested. The assumption that all labs have autosampler capability is dubious. The "10 hour" number could also be an under-estimate of the method set-up time, as the 10- hour estimate assumes the preparation goes as planned. TGA analysis does not require the extensive preparation steps/standards that GC/FID analysis requires.

AQMD Response
Method 313-L does not mention running "seven standards" with every batch; therefore subsequent comments and calculations based on this assumption significantly overstate required time. Instead of requiring "13 runs", the method only requires one calibration check, one blank,

a matrix spike and duplicate per batch, or 5 runs. After these instrument checks, ten samples are analyzed. Because the instrument checks are divided among many samples, the analysis time reduces to approximately 105 minutes per sample. TGA, on the other hand, requires well over two hours for each sample; and because an autosampler cannot be used for TGA analysis, this impacts staff time directly.

Comment
Following the method as written, final calculations require at least 10 mathematical steps to arrive at an answer. Calculations require the generation of a statistics package and the use of linear regression. Results may be affected by how the analyst chooses to perform the regression (dropping the y-intercept or forcing the equation through zero).

Response
These kinds of calculations should be within the capacity of GC laboratories experienced with ASTM simulated distillation and similar methods. The calculation of linear regressions, for example, is a routine part of GC analysis and can be accomplished either using standard chromatography software or functions built into modern spreadsheets. In any case, if the participating laboratory does not want to develop its own spreadsheets, the AQMD will supply them.

ILMA Reply
Relative to the TGA method (ASTM E1868-10), the calculations required to arrive at an answer for Method 313-L are clearly more complex and subject to more opportunities for error. The fact that AQMD staff has to help individual labs to perform calculations by creating spreadsheets is self-evidence of the highly complex nature of the method. AQMD lab staff has revised the VOC calculations several times because of inconsistent instrument response. AQMD lab staff also has attempted to apply correction factors to data generated by outside labs in order to obtain the results they desired to see. These calculations involve operator judgment, which is always a problem for standardized methods.

AQMD Response
Calculating a calibration curve and checking to see if the curve and instrument is stable from batch to batch is a routine part of gas chromatography. One of the reasons for providing a spreadsheet was to simplify review by creating a standard format.

Comment
The method calls for ramped flow rates, which require electronic flow control (EFC). Many older or entry level GC's in use today do not have this capability, and thus, some labs will be forced to alter the method to suit available hardware. This has been shown to lead to large discrepancies in the retention times of the marker compound (methyl palmitate). During the initial Method 313-L robustness testing, retention times for methyl palmitate among the participating labs ranged from 25 –42 minutes, which is an enormous spread in GC terms.

Response
Most GC methods (including this one) assume uneven instrument capabilities. This is why most GC methods (including ASTM GC methods) either "recommend" or list "typical" instrument

parameters rather than "require" them; and focus instead on performance check standards to validate final results. Retention time markers are a common form of quality control which specifically allow for variations in flow, temperature, column performance etc. (deliberate or otherwise) without disturbing the final result. Whether the observed retention time spread is "too large" to generate a reproducible result is one purpose of the interlaboratory study, and should not be assumed in advance. So far, results do not support concerns about the range of methyl palmitate retention times. However, staff is also continuing to evaluate other Method 313-L endpoints to address other issues.

ILMA Reply

There is a large difference between "uneven instrument capabilities" resulting in fluctuations of retention times by 1 – 5% among labs, and the results observed for the inter-lab study, in which retention times were found to differ by as much as 30 – 40%. The method, as written, assumes advanced GC capabilities that all labs do not have, and the results of the initial inter-lab study clearly reflect this. The variations considered acceptable by the AQMD lab staff may be okay for analysis of organic compounds of a similar chemical nature (hydrocarbons, carboxylic acids, carboxylic esters, amines, and fatty alcohols), but they become unacceptable when analyzing a complex mixture of organic compounds.

AQMD Response

One point in ILMA's initial comment needs clarification: Method 313-L does not require "ramped flow" or "advanced capabilities". Different laboratories did indeed choose to utilize somewhat different elution conditions. But since they all used the same column, the various compounds all eluted in the same order, even if they didn't elute at the same time from lab to lab. In other words, compounds which eluted after the retention time marker always eluted after the retention time marker, whether that marker eluted at 25 minutes or 40 minutes. Therefore, the same compounds were classified as VOC (or non-VOC) no matter where the actual endpoint occurs, and the results were insensitive to actual marker compound elution time.

Comment

Under Method 313-L parameters, the signal: noise (S/N) ratio for 60 and 100 second oils is relatively low. Additionally, natural oils do not elute as sharp, clean peaks, but as broad unresolved "humps". In practice, this means that such oils are difficult to clearly distinguish from the electrical noise generated by the instrument (a.k.a. column "bleed"). This results in ambiguity as to how to properly place the baseline for oil-based samples, and thus how to correctly integrate the chromatogram. Baseline placement has a profound effect on the final calculated results for oil based samples, as evidenced by data generated during the robustness testing:

Table 1 –Perceived Effect of Baseline Placement on Robustness Testing Results

Lab	Baseline Type	Result (g/l)	Comments
1	Flat	240-251	Includes column bleed, leads to high results
2	Flat	277	Includes column bleed, leads to high results
3	Angled	67-73	Low results due to failure to included all hydrocarbon peak area
4	Curved (S-shaped)	133-185	Manually fitted; best compromise between flat and angled baseline

Response
There are several issues folded into one comment.

Signal/ noise: AQMD has noted that some laboratories appear to have higher baseline signals and less sample response. The current Method 313-L method has been modified to increase the sample amount. Part of this problem may have resulted from suboptimal injection port liners, which have been more exactly specified (see below)

Column bleed: Inter-sample solvent injection has eliminated carryover; some laboratories appear to have a baseline rise of unknown origin, which the AQMD is working to understand and eliminate. In any case, the current version of Method 313-L does not include the area of baseline rise.

Baseline placement: The appropriate placement of the baseline is unambiguous- It is the blank baseline at the beginning of the run. In this regard, both the baseline difficulties and the baseline placement in Method 313-L are similar to ASTM simulated distillation methods and other GC methods of natural products. These difficulties have been successfully negotiated by many laboratories performing similar methods.

ILMA Reply
Signal/ noise: This does not address the fundamental issue that natural oils are extremely difficult to handle quantitatively and reproducibly by GC/FID. Specifying injection liner type is good practice, though the type of liner chosen will have little to no effect on overall difficult to handle peak shape generated by natural oils.

Column bleed: Inter-sample solvent injection may reduce carry-over, but its elimination cannot be guaranteed. The baseline will rise some finite amount with increasing oven temperature, no matter what is injected. For samples of low signal/noise ratio, accidental inclusion of this column bleed or electrical noise by inexperienced outside laboratories is a real concern that should not be overlooked by AQMD lab staff. Such practice would lead to artificially high calculated VOC values.

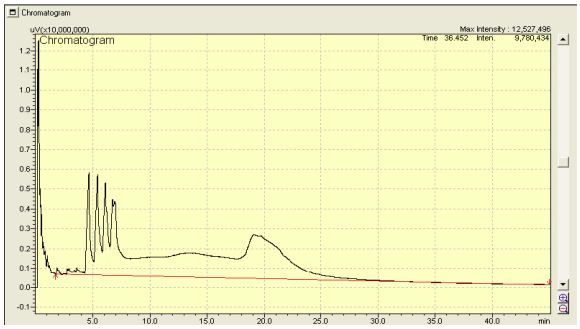
Baseline placement: Upon close inspection of the solvent blank baseline, an S-shaped curve may be observed. Placement of the baseline at the lower or higher end of the curve will affect the final results for samples of low signal/ noise ratio. There is no provision to account for this in the method as written, and thus is considered ambiguous. The attempt at baseline manipulation does not consider sample influence on the FID detector response. The FID is a flame, anything which disrupts the flame impacts the signal response.

AQMD Response
Signal/ noise: “Difficult” peaks shapes are an expected feature of natural oil analysis such as lubricants, diesels, bitumens, food oils, residues, crude oils and similar products. This problem has been encountered and resolved in chromatography methods promulgated by ASTM and other entities:

ASTM D6074 - 08 *Standard Guide for Characterizing Hydrocarbon Lubricant Base Oils* references,
ASTM D2887 - 08 *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*
ASTM D3524 - 04 *Standard Test Method for Diesel Fuel Diluent in Used Diesel Engine Oils by Gas Chromatography*
EPA 8270D *Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry*.

For example, when analyzed by *ASTM D 5307 Simulated Distillation Analysis,* heavy bitumen produces the following trace (reproduced from the Shimadzu application website)

Simulated Distillation Analysis of Heavy Canadian Crude Oil by ASTM D 5307



(This sample has been spiked with C14 through C17, seen on the left, as retention-time markers.) Because of the commonality of the problem, detection and integration of merged peaks is supported by all chromatography manufacturers.

Column bleed: ILMA has concerns about being able to distinguish baseline rise from sample VOC. There are several solutions to this issue. The first is to eliminate baseline rise as much as possible. Just as TGA will not work properly if it has dirty supply gases, an un-calibrated balance or thermometer, or dirty sample pans, a GC will not work well if it isn't properly maintained. In GCs, baselines can rise for a number of reasons including dirty supply gases, leaks, column bleed and sample carryover. These problems are eliminated using proper chromatography practices. A second part of the answer is to transfer sufficient sample onto the column such that the sample signal is high enough to be distinguishable from baseline rise. Method 313-L has been modified to increase the prepared sample concentration. The last part of the solution is to perform a blank injection for each batch, as required by Method 313-L. This step allows the baseline to be evaluated for suitability.

Baseline placement: There are several possible methods for drawing baselines, and these vary between instruments. If the baseline is flat, a straight line is sufficient. But in the case of non-linear baselines, chromatography software includes a baseline subtraction option. (A few vendors require a SIMDIS package for this feature). However, since the temperature range of the current Method 313-L analysis is limited, baseline subtraction should not be necessary.

Comment
Column (DB-624) is classified as mid-polar, and is thus not suitable for performing a simulated distillation, in which compounds are separated strictly by boiling point. The use of a column such as DB-624 introduces a secondary retention mechanism into the chromatography (dipole-dipole interactions). The analysis of MWF's, which contain polar compounds, will result in a separation that is influenced by both chemical structure (dipole moment) and boiling point.

Response
The column was not intended to perform simulated distillation. The specified column helps resolve exempt compounds from VOC compounds, allowing more accurate analysis. In addition, there is no reason to assume that a "boiling point" column is more reflective of real-life evaporation. In fact, since real-life evaporation involves chemical structure (dipole-dipole interactions), an argument could be made that DB-624 is more reflective of real-life conditions. (ASTM D7398, Standard Test Method for FAME Boiling Point Range by GC). From further work with the method, we have found that this column can, in fact, reproduce both Method 24 and TGA evaporative methods reasonably well.

ILMA Reply
The method as written clearly does not reproduce the approved TGA method (which has been demonstrated to reflect long term evaporation in an oven), as evidenced by the artificially high VOC values obtained for semi-volatile oils. The statement "The column was not intended to perform simulated distillation" indicates an improper understanding of GC instrumentation. The column is actually being used to replicate and perform simulated distillation, with chemical adsorption/desorption interactions also being involved. The use of a marker compound to differentiate a VOC from a non-VOC compound, with the stipulation that ALL compounds that elute prior to the marker compound are VOC in nature, replicates distillation. The adsorption/desorption characteristics of the column stationary phase are not the same as the dipole-dipole interactions of air atmosphere chemical volatilization.

AQMD Response
The original Method 313-L did not reproduce the currently-approved TGA method because it was written to reproduce the national standard, EPA Method 24. The revised Method 313-L, however, does compare well with the approved TGA in samples tested so far.

Comment
Methyl palmitate is a poor choice of marker compound, for the secondary interaction reasons given above, and its choice has never been clearly explained. In essence, methyl palmitate (being a polarizable compound) is retained for a longer time period (due to secondary column interactions) than a hydrocarbon of comparable molecular weight (C19H40). The end result is an artificially large "retention window" in which VOC is calculated, that is not representative of a true boiling point separation.

Response
Again, since the column was not chosen for boiling point determination, neither was the endpoint. The endpoint was determined as the closest approximation of EPA Method 24 results.

Staff is currently evaluating alternative endpoints to assess if greater conformity with VOC results, as determined by evaporation rate studies and TGA, is achievable.

ILMA Reply
The behavior of methyl palmitate under the conditions of EPA 24 and on a semi-polar GC column of arbitrary temperature conditions has a tenuous correlation, if any. It is clear from the initial inter-lab studies that using methyl palmitate as the key retention time marker results in calculated VOC values for semi-volatile oils that are significantly higher than results obtained by the Dodge evaporation study or by the approved TGA method. Investigation of alternative marker compounds would certainly improve the method, though would likely require months of additional research and data generation.

AQMD Response
The originally written Method 313-L does not reproduce the evaporation study or the TGA study because it was designed to reproduce the national standard, EPA Method 24. While Method 313-L and Method 24 match each other, neither method matches the evaporation study or the TGA method. The advantage of Method 313-L, however, is that it is possible to review the data to determine if a new endpoint will reproduce evaporation study and TGA results. This has already been done; when AQMD data is reprocessed using a new marker compound, the results compare well with evaporation study and TGA results.

Comment
Detector response factors for non-hydrocarbons are mentioned, but never clearly addressed. Given the vast amount of volatile/semi-volatile raw materials that could conceivably be present in a given MWF, the chance for erroneous results appears to be high. These errors could be compounding with more complex fluids.

Response
The errors, if there are any, will be biased low, in favor of metalworking fluids, since the presence of heteroatoms (oxygen, nitrogen, sulfur, and chlorine) reduces sample response. However, in typical metalworking fluid compounds, these heteroatoms are expected to have only a small negative effect. ("Modern Practice of Gas Chromatography" Robert Lee Grob, Eugene F. Barry p.303, “Effect of Molecular Structure Upon the Response of the Flame Ionization Detector”, M Kallai, J. Balla, Chromatographia 2002).

ILMA Reply
The unpredictable GC response of the thousands of possible compounds that might be present in a given metalworking fluid adds yet another layer of uncertainty to the method, and introduces additional sources of error to Method 313-L. As many labs would be performing the analysis on fluids of unknown composition, there is no practical way to account for such error during routine testing. FID detector response is a very real problem, not all compounds produce linear FID response. ILMA is concerned with the generalized opinions expressed in the AQMD response, and the assumptions being made.

AQMD Response
FID (detectors) are widely known for their linearity over several orders of magnitude, and laboratory results indicate that participating laboratory detectors were linear from approximately 200 ppmv to at least 10,000 ppmv. Since sample responses never exceeded 5000 ppmv it is unlikely that FID linear range would be exceeded.

FIDs are also widely known for their predictable response, earning them a reputation as "carbon counters". This is due to the fact that all carbon atoms eventually form the same detected specie in a FID flame, no matter what the source molecule. Nonetheless, carbon response can be influenced by adjacent non-carbon atoms. Besides their base oils (for which FIDs are ideally suited) lubricants also include additives which may contain oxygen, chlorine, sulfur, nitrogen, calcium, zinc, phosphorous or other non-carbon atoms. Correction factors for various non-carbon atoms are widely available; they have allowed AQMD staff to estimate a negative bias of 10% or less for chlorinated paraffins containing 55 percent by weight chlorine.

Comment
Split injection technique does not address the possibility of split discrimination in the injector. Discrimination is a phenomenon that can occur for wide boiling point mixtures in which the entire vaporized sample is not swept onto the column homogenously.

Response
AQMD has noted that some laboratories appear to have had injection irreproducibility and some discrimination. To obviate any potential problems, the method has been modified to specify a double-tapered, glass-wool filled, passivated injection port liner. This is very much like specifying the type of pan required for TGA analysis. However, embedded quality control in Method 313-L will indicate whether injection port discrimination is taking place. Therefore, the GC method is both self-reporting and self-correcting.

ILMA Reply
Split discrimination is a function of the injection technique itself, not the type of liner used. Discrimination (by definition) is an indeterminate source of error that could also be a function of injection technique. Normalizing liner type is good practice, but cannot eliminate split discrimination, particularly for wide boiling point mixtures. The notion that the GC method is self-reporting and self-correcting is debatable, at best. In order to properly determine VOC content by GC analysis, a split injection should not be utilized. ALL the volatile compounds should pass through the column for detection/analysis. A split injection technique could discriminate and "lose" some highly volatile compounds, thus skewing the results.

AQMD Response
Split injection is a technique which transfers only a portion of injected sample onto the GC column, and vents the remainder. This is to prevent column overloading. Sample discrimination can occur when disproportionate amounts of high (or low) molecular compounds are vented, enriching one group of compounds relative to another. If no discrimination is taking place, equal amounts (by weight) of C6 to C15 standards should produce equal-sized peaks. This can be easily checked using the C6 through C15 calibration slopes. Sample discrimination can be detected easily.

Comment
Thick fill columns (1.00 µm) are prone to bleed more than the more common 0.25µm columns. This effect increases over time as the column ages and the temperature is repeatedly cycled. This will exacerbate baseline placement issues discussed above.

Response
The column in the AQMD laboratory has been in use for two years, analyzing lubricants and paints and coatings, and has not deteriorated in performance or developed column bleed. Analysis blanks further address the issue of baseline drift and is therefore added to Method 313-L protocol.

ILMA Reply
The degradation of GC columns over time with repeated use and temperature cycling is an accepted fact. Injection of real-world samples that may contain more aggressive compounds (inorganic acids/bases) than have been studied in the AQMD labs will exacerbate degradation, and may lead to baseline and/or column problems that staff has thus far not anticipated. Column degradation is a very real concern, especially when the cost per column is rather high. One cannot extrapolate column life expectancy based upon analysis of simple organic mixtures.

AQMD Response
ILMA's implied call for a thin-film column is at odds with their call for splitless injection, since a thin-film column would be overloaded.

Comment
When real samples are analyzed, many high molecular weight components (surfactants, polymers, polyol esters, sulfonates, etc.) will not elute from the column and remain trapped in the inlet liner or at the head of the column. This may lead to "ghost peaks" in subsequent runs, which in effect is the appearance of compounds not present in sample proper, but slow volatilization of the "leftovers". Single inter-run "bakeouts" may not fully address this issue.

Response
The current method requires an inter-sample solvent injection, which eliminates carryover in a normally clean system. However, as with any analysis of complex samples, the injection port liner should be replaced and possibly the first loop of column trimmed. AQMD does replace injection port liners about once every six months, but has not yet had to either trim or replace a column. Laboratories are also encouraged to perform periodic maintenance which may include and overnight bakeout to clean out contamination.

ILMA Reply
Again, inter-sample solvent injection is helpful, but cannot guarantee elimination of sample carry-over. This "hope for the best" approach, particularly when dealing with contract laboratories unfamiliar with lubricant/metalworking fluid formulations, may lead to chromatography problems and artificially high calculated VOC values that will not be immediately obvious to the inexperienced analyst. Sample carry-over is one problem, another problem is reactive interference. Reactive interference occurs when the residue left in the injection liner from one sample adversely reacts with the compounds of a different sample when the new sample is injected for analysis.

AQMD Response
Regular injection of blanks would flag long-term contamination, if it occurs. Reactive interference would be suspected when very light compounds appear in a chromatogram, indicating sample fracturing. So far, this problem hasn't been observed with lubricant samples. However, AQMD recommends changing injection port liners according to manufacturer recommendations.

Comment
Automated integration performed by a given chromatography software program, will have a difficult time handling the complex baseline placement issues for natural oils described above. The notion that any and all contract analytical labs will successfully navigate this issue (via manual integration) is hopefully optimistic, at best.

Response
Method 313-L contains sufficient quality control to determine whether integrations have been performed properly.

ILMA Reply
Method 313-L, when performed as written with good analytical practice, is clearly not as efficient as the TGA method. The embedded quality control procedures in Method 313-L are useful in detecting abnormalities in individual injections, but do not account for proper integration of oil-based unknowns, the most critical issue at stake in the analysis. Proposed changes to Method 313-L will require months of additional study/research to determine their effectiveness at mitigating the myriad problems with the method staff has admitted to. This is an unnecessary expense of time and money, when a rapid, reproducible, and accurate TGA method has already been developed and validated.

AQMD Response
The issue of integration and efficiency has been addressed in previous comments. Improvements to the method based on the first interlaboratory have been incorporated, much like the changes that were made to the TGA method. The last revision to Method 313-L was to parallel TGA results. The remaining step is to determine how well the revised method will work in other laboratories. Since the first round met program goals (with the exception of one laboratory) and revisions made the method simpler and more accurate, it is expected that the second interlaboratory evaluation will prove to be successful. It also should be pointed out that should the development and validation of Method 313-L be completed, it would be staff's intent to include Method 313-L in the rule as an alternative to the TGA-based test method and not as a substitute to it. End users that find the TGA method preferable to work with should be able to continue employing it as their test method of choice.

In summary, Method 313-L is at least as efficient as TGA in terms of output. But Method 313-L includes quality control procedures which reveal whether the final results are accurate. In addition, the Method 313-L shows greater potential for analyzing water-based samples more accurately than the TGA method, which depends on a secondary water analysis which has not been validated for metalworking fluids. Proposed changes to the Method 313-L protocol are expected to mitigate many of the concerns listed above. This protocol will be revised prior to

initiating another round robin, and staff will share any changes with ILMA and other stakeholders.